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Final Report

ONR Grant No. N00014-91-J-1269

December 1, 1990 to November 30, 1993

"Novel Materials"

May 12, 1994

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work performed under the direction of

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This is the final report on a project funded for 3 years by ONR. The project was very successful; it resulted in the discovery of many new solid state ternary nitrides. Since there were so few ternary nitrides known, and since many of the binary nitrides, such as TiN, AlN and Si₃N₄, are so technologically useful, our aim was to explore the synthesis, structural chemistry and properties of ternary nitrides. Prior to our work very few ternary nitrides, other than those formed by alloying binaries and having simple binary like structures, were known. We have shown that there is indeed a very large class of such ternary nitrides.

We discovered that there is a very large class of ternary nitrides of general formula $M_xT_yN_z$, where M is an electropositive metal (alkali or alkaline earth metal), T is a transition metal or post-transition main group metal, and N is nitrogen. Such compounds exist for example when $M = Ca$ for all T, with only a few exceptions. These compounds have structures and properties quite unlike those of oxides, sulfides, phosphides or carbides - all those elements that are neighbors to nitrogen. In general when the compounds are in the highest oxidation state attainable in a N₂ atmosphere, the coordination number of the T cation is small, generally 2 or 3. Sometimes oxidation states that are rare or non-existent in other compounds are produced; for example, Ni(I) is present in compounds such as CaNiN.

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The reaction chemistry of nitrides also had to be developed. We prepared such phases by several methods including: reaction of pressed powders of binary nitrides in N_2 gas, reaction of metals or ternary oxides with NH_3 , and the use of super critical NH_3 at high temperatures (up to $800^\circ C$). General thermodynamic principles were developed for the prediction of useful precursor solid state materials in NH_3 flow reactors. This predictive scheme is particularly useful for oxide precursors, since the thermodynamics of oxides is quite well explored. We predicted that in general oxide compounds containing electropositive metals (alkali, alkaline earth and rare earth metals) will NOT form ternary nitrides when reacted with NH_3 , while all other oxides may well form such ternary phases.

We were the first scientists in the US to explore these materials, but two other chemists in Germany (H. Jacobs and R. Kniep) at the same time began research programs that are parallel to our program. Our work combined with their findings shows that there are indeed a huge number of ternary compounds of the type anticipated in our original proposal. More recently, several US research groups have begun research in this same area since it seems so ripe for discovery.

The research supported by ONR resulted in the publication of 18 research papers and was the main focus of the work reported in 4 PhD theses. The support of ONR in this research was greatly appreciated.

Publications Resulting from ONR Support:

1. "Solid State Chemistry: A Rediscovered Chemical Frontier", F.J. DiSalvo, Science, 247, 649 (1990).
2. "A Small, Inexpensive Apparatus for the Determination of the Density of Powdered Materials", M.Y. Chern, R.D. Mariani, D.A. Vennos and F.J. DiSalvo, Rev. of Scientific Instruments, 61, 1733 (1990).
3. "Synthesis, Structure, Electrical and Magnetic Properties of $CaNiN$ ", M.Y. Chern and F.J. DiSalvo, J. Solid State Chemistry, 88, 459 (1990).
4. "Synthesis, Structure, and Properties of Ca_2ZnN_2 ", M.Y. Chern and F.J. DiSalvo, J. Solid State Chemistry, 88, 528 (1990).

5. "Synthesis, Structure, and Properties of a New Ternary Metal Nitride: Ca_3CrN_3 ", D.A. Vennos, M.E. Badding and F.J. DiSalvo, Inorganic Chemistry, 29, 4059 (1990).
6. "Synthesis, Structure and Properties of Anti-perovskite Nitrides Ca_3MN , with $\text{M} = \text{P, As, Sb, Bi, or Ge, Sn, and Pb}$ ", M.Y. Chern, D.A. Vennos and F.J. DiSalvo, J. Solid State Chemistry, 96, 415 (1992).
7. "The Structural Distortion of the Anti-perovskite Nitride AsNCa_3 ", M.Y. Chern, F.J. DiSalvo and J.B. Parise, J. Solid State Chemistry, 96, 426 (1992).
8. "The Structure of Ta_3N_5 at 16K by Time-of-Flight Neutron Diffraction", N. Brese, M. O'Keeffe, P. Rauch and F.J. DiSalvo, Acta Cryst., C47, 2291 (1991).
9. "Synthesis, Structure and Properties of a New Intermetallic Compound, $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$ ", D.A. Vennos, M.E. Badding and F.J. DiSalvo, J. Less Common Metals, 175, 339 (1991).
10. "Structure of Lithium Niobium Nitride", D.A. Vennos and F.J. DiSalvo, Acta Cryst., C48, 610 (1992).
11. "Synthesis and Characterization of a New Ternary Nitride, Ca_3VN_3 ", D.A. Vennos and F.J. DiSalvo, J. Solid State Chemistry, 98, 318 (1992).
12. " LiMoN_2 : The First Metallic Layered Nitride", S.H. Elder, L.H. Doerrer and F.J. DiSalvo, Chem. of Materials, 4, 928 (1992).
13. "Ambient Pressure Synthesis of Ternary Group (V) Nitrides", P.E. Rauch and F.J. DiSalvo, J. Solid State Chemistry, 100, 160 (1992).
14. "The Synthesis and Structural Characterization of Na_3WO_3 ", S.H. Elder, F.J. DiSalvo, J.B. Parise, J.A. Hriljac and James W. Richardson, Jr., J. Solid State Chemistry, 108, 73 (1994).
15. "Synthesis and Neutron Diffraction Study of Na_3WN_3 and Na_3MoN_3 ", P.E. Rauch, F.J. DiSalvo, N.E. Brese, D. Partin and M. O'Keeffe, to be published in J. Solid State Chemistry.

16. "Thermodynamics of Ternary Nitride Formation: Application to LiMoN_2 , Na_3WN_3 and $\text{Na}_3\text{WO}_3\text{N}$ ", S.H. Elder, F.J. DiSalvo, L. Topor and A. Navrotsky, Chemistry of Materials, 5, 1545 (1993).
17. "Synthesis, Structure and Properties of M_2NiN_2 (M = Sr and Ba)", G.R. Kowach, N.E. Brese, U.M. Bolle and F.J. DiSalvo, in preparation.
18. "New Cerium Nitride Chlorides: $\text{Ce}_6\text{Cl}_{12}\text{N}_2$ and CeNCl ", Grant M. Ehrlich, M.E. Badding, Nathaniel E. Brese, Steven S. Trail and F.J. DiSalvo, J. Alloys and Compounds, 206, 95 (1994).

Theses Resulting from ONR Support:

1. Ming Yau Chern (1991) "Synthesis, Structure, and Properties of New Ternary Calcium Nitrides"
2. Paul E. Rauch (1991) "Synthesis and Structure of New Ternary Nitrides and Chalcogenides"
3. Deborah A. Vennos (1992) "An Investigation of New Nitrides: Synthesis, Structure, and Properties"
4. Scott H. Elder (1993) "The Synthesis and Study of New Ternary Nitrides and Oxynitrides Prepared from the Ammonolysis of Ternary Oxides"

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